

ABUNDANCE, SIZE AND ORGANIZATION OF AROMATIC MOIETIES IN INSOLUBLE ORGANIC MATTER OF ORGUEIL AND MURCHISON METEORITES S. Derenne¹, J.-N. Rouzaud², J. Maquet³, C.

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Introduction: The primitive carbonaceous chondrites contain substantial amounts of carbon (up to 3%), mostly as macromolecular insoluble organic matter (IOM). This IOM is considered as a record of interstellar synthesis and may contain precursors of prebiotic molecules possibly deposited on earth by meteoritic bombardments. For these reasons, chondritic IOM has been raising interest for long and it is now well established that the chemical structure of this macromolecular material is based on aromatic moieties linked by short aliphatic chains and comprising substantial amounts of heteroatoms. However, due to limitations on analytical tools, its precise chemical structure and especially the abundance and size of the aromatic moieties are still a matter of debate.

To characterize the aromatic units in chondritic IOM is important to determine the conditions involved in space in their synthesis. Indeed, likely due to their high stability, polyaromatic structures are among the most abundant and widespread organic structures in the universe and may represent a link between the interstellar medium and the solar system. In the present work, we used two non-destructive techniques, namely solid state ¹³C nuclear magnetic resonance (NMR) and high resolution transmission electron microscopy (HRTEM) to determine the abundance and the main features of the aromatic units in the IOMs isolated from two carbonaceous chondrites, Orgueil and Murchison using the classical HF/HCl treatment.

Results. *Solid state ¹³C NMR* is a powerful tool to determine the nature and environment of carbons in organic macromolecules. Due to the low natural abundance of the ¹³C isotope, enhancement of the signal provided by the cross-polarization sequence (CP) is commonly used. The CP sequence involves magnetization transfer from the abundant proton reservoir to the less abundant ¹³C one, during contact time. Due to this transfer, carbons far from protons, such as those in the core of large polyaromatic units cannot be detected by CP NMR. Moreover, due to differences in CP dynamics between the different types of carbons (e.g. protonated or not), spectra recorded at different contact times exhibit differences in carbon distribution. As a result, quantitation of resonant carbons can only be derived from a series of spectra recorded with variable contact times, so as to derive absolute magnetizations, proportional to the number of such carbons. An alternative to the CP sequence is the single pulse one (SP) in which the carbons are directly

detected, hence the lack of drawbacks related to magnetization transfer but also a much lower signal to noise ratio.

Spectra of the IOM from Orgueil and Murchison using CP sequence and a "classical" contact time of 1 ms, led to a rather low aromaticity for these samples (0.4-0.5), suspected to be underestimated [1]. These IOMs were recently revisited using the CP sequence with variable parameters including contact times thus yielding absolute magnetizations [2]. Comparison between NMR-derived composition and data from elemental analysis revealed that a large part of the carbons of these IOMs are not detected by CP NMR. Two contrasted types of aromatic moieties could be, a priori, put forward to account for this lack of detection: either large polyaromatic units or rather small aromatic units provided they would only contain few peripheral hydrogens, i.e. they would be highly substituted. The latter assumption was favoured in this study which also revealed a high level of branching in the aliphatic chains of the chondritic IOMs. When these non-detected carbons are taken into account, aromaticities of 0.6 to 0.8 can be calculated. Spectra of Murchison IOM using both cross polarization (CP) and single pulse (SP) sequences [3] confirmed the occurrence of highly substituted small aromatic units, cross-linked by short, branched aliphatic chains, the aromaticity being 0.61-0.66. Based on the similarity between the SP spectrum and that obtained with CP at long contact time (4 ms), the authors (i) concluded there was no "invisible" carbon to the CP NMR for Murchison IOM at that contact time and (ii) recommended to use such long contact times to derive quantitative data from CP spectra.

In the present study, spectra of the IOM of Orgueil were recorded with SP and CP sequences, 12 contact times (ranging from 0.5 to 9.6 ms) being used in the latter case. The carbon distribution derived from the SP spectrum (revealing an aromaticity of 0.69) was compared with those obtained by CP from the absolute magnetizations on the one hand and from each contact time on the other hand. It thus appears that (i) numerous aromatic carbons are indeed not detected by CP and (ii) increase in contact time (> 2 ms) leads to lower detection of the aliphatics due to their relaxation (in the rotating frame), hence apparent aromaticity fraction closer to that derived from SP although similarity could not be reached with Orgueil for 4 ms (aromaticity of 0.43) and even for 9.6 ms (0.50). Such similarity is therefore sample-dependent and it clearly

AROMATIC MOIETIES IN INSOLUBLE ORGANIC MATTER OF METEORITES. S.Derenne et al.

appears that in spite of its low sensitivity, only SP spectra can lead to quantitative data on polyaromatic macromolecules as those present in chondritic IOMs.

HRTEM. The aforementioned results raised the question of the size of the aromatic units in the chondritic IOM. As already mentioned, assessing this size is important for several reasons and especially to test the occurrence of a link between the solar system and the interstellar medium since the size range of PAHs in the latter medium has been assessed. HRTEM in the lattice fringe mode is a powerful technique for direct observation of polyaromatic skeletons and thanks to the recent development of an image analysis processing [4], the main structural parameters of the aromatic units can now be determined. The distributions obtained for the diameters of the aromatic units show an average of 0.86 and 0.67 nm for Orgueil and Murchison, respectively. These values correspond to 3 to 4 rings in diameter, i. e. a total number of ca. 10-15 rings. HRTEM of chondritic IOM therefore ascertains the small size of the polyaromatic units. Moreover, a rather poor organization is revealed by the relative abundance of isolated layers, i.e. polyaromatic layers not included in coherent domains formed by the stacking of layers. When these coherent domains are considered, their diameter, height, interlayer spacing and number of layers per stack were also determined. Taken together, all these parameters pointed to a low level of organization, especially for Murchison IOM.

A minimum size of 60 carbon atoms, i.e. about 5 rings in diameter, was assessed for the polyaromatics in the interstellar medium [5]. This size is substantially larger than that observed in the present study for the aromatic moieties of the chondritic IOMs. Such a difference may be due to different organosynthetic pathways for aromatic moieties in meteorites and in the ISM. However, the preservation of small aromatic units in the chondritic OM cannot be excluded. Indeed, laboratory experiments on photon irradiation of polyaromatic hydrocarbons (PAHs) showed that the smallest PAHs will preferentially dissociate rather than relax by infrared emission, suggesting that in the interstellar medium, the smallest aromatic units are destroyed by UV photolysis.

However, if PAH accumulation on grains is faster than photodissociation, these small units being then protected from UVs should escape degradation and thus predominate in chondritic IOMs. This scenario is illustrated on figure 1.

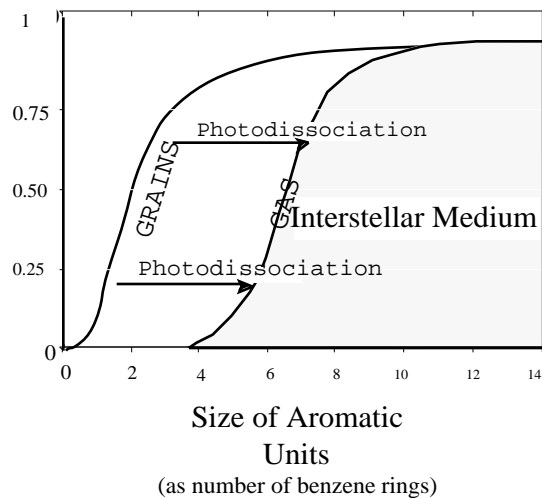


Figure 1 : Cumulative fraction of the abundance of the aromatic moieties as a function of their diameter. The left-hand line is derived from experimental data. The right-hand line, deduced empirically from the left-hand one, illustrates the possible distribution of aromatic units in the ISM; it is supposed to represent the distribution of the aromatic units after UV photodissociation and accounts for the lack of detection of the smallest moieties in the ISM.

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